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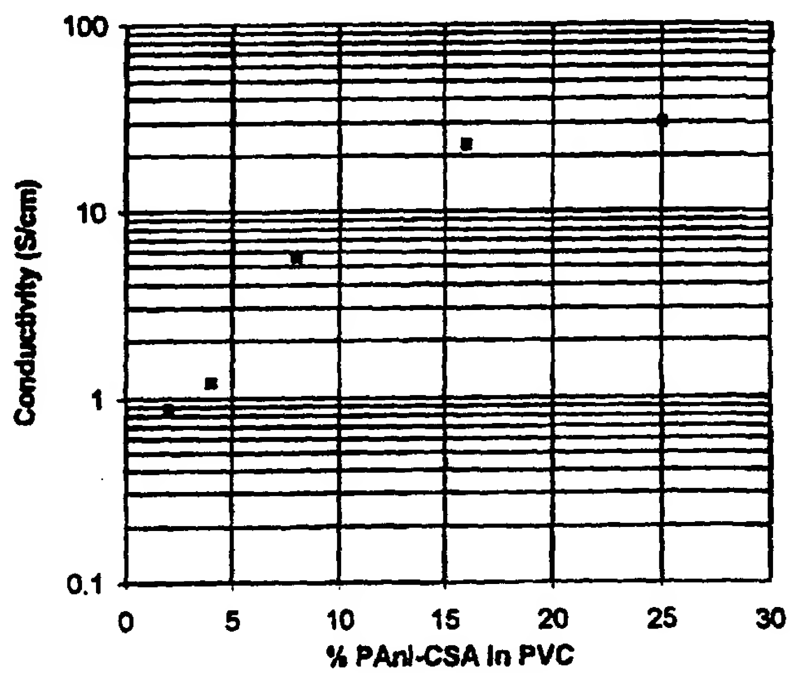
(54) Title: CONDUCTING POLYMER COMPOSITE



(57) Abstract

An electrically conductive or semi-conductive composite material formed from a plurality of thermoplastic particles that have been pre-coated with a conducting or semiconducting polymer and brought together under conditions of appropriate temperature so the the conducting or semiconducting polymer forms a network through the composite.

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CONDUCTING POLYMER COMPOSITE

Field of the Invention

The present invention relates generally to composite materials consisting of conventional thermoplastics and intrinsically conducting polymers (ICPs) and in particular to an electrically semi-conducting or conducting composite material and methods for forming same. The composite material has potential application in a wide range of devices including microwave devices, pressure sensors, temperature sensors, cable shielding, electromagnetic shielding, anti-static materials for computers and other applications, radar-absorbing materials, light weight battery electrodes, high-power junction devices, corrosion resistant electrodes and corrosion resistant cable termination coatings.

Background Art

A number of intrinsically conducting polymers have now been known for well over a decade. One of the most extensively characterised conducting polymers is polyacetylene. This polymer possesses a backbone with a high degree of unsaturation leading to π-orbital overlap and electron delocalisation. This delocalisation allows the polymer to possess a quite remarkable electrical conductivity when compared with traditional insulating polymers. The structure of this polymer is, however, quite unstable.

Another common class of intrinsically conducting polymers are the polyheterocyclics, such as polypyrrole and polythiophene. In the case of polypyrrole, the repeat unit of this polymer is comprised of a 5-membered cyclic ring with two delocalised π bonds and a nitrogen heteroatom. Polypyrrole when produced using an electrochemical process can form a free standing film with an electrical conductivity as high as 100 S/cm. Polyheterocyclics have an improved stability in comparison to polyacetylene, the improved stability being provided by the aromatic nature of the heterocyclic ring which prevents loss of π bond unsaturation.

Despite there being a quite large number of postulated applications for such polymers, their use to date has been limited by poor environmental stability and poor mechanical properties. Poor processability and poor solubility have also prevented processing of the polymers using traditional polymer processing techniques.

The blending of conventional thermoplastics with intrinsically conducting polymers leads to processable semi-conducting thermoplastics. Previously, this has been achieved by intimate mixing of thermoplastics with intrinsically conducting polymers either by solution processing (for example see A. Andreatta and P. Smith, Synthetic Metals (1993), 55-57, 1017) or by direct blending (for example see L.W. Shacklette, C.C. Han and M.H. Luly, Synthetic Metals (1993) 55-57, 3532). These methods result in a semi-conducting or conducting thermoplastic composite which requires at least 15% w/w intrinsic conducting polymer to achieve electrical conductivities comparable to that of the pure intrinsically conducting polymer. This is due to the nature of the microstructure of blends arising from these procedures. These methods of processing result in conduction through a dispersed phase consisting of flocculated structures. This behaviour results from what is termed a percolation network and is analogous to that observed when a thermoplastic is loaded with conventional conductors (such as silver particles) or semi-conductors (such as carbon black).

It has been shown that under certain conditions, solution processing can lead to a network structure (for example see C.Y. Yang, Y. Cao, P. Smith and A.J. Heeger, Synthetic Metals (1993) 53, 293) in a blend of conventional thermoplastic with an intrinsically conducting polymer. The network structure apparently depends upon the miscibility of the solvent used for the thermoplastic and that used for the intrinsically conducting polymer. This method results in a composite material possessing a significant electrical conductivity at a low level (<1% w/w) of intrinsically conducting polymer but only yields thin film materials.

It has also been shown that polyethylene films, the surface of which has been sulfonated, can be coated with pyrrole followed by a chemical oxidative polymerisation resulting in a conducting polymer coating on the surface of the film (for example see K. Yoshino, X.H. Yin, S. Morita, Y. Nakanishi, S. Nakagawa, S. Yamamoto, T. Watanuki and I. Isa, Japanese Journal of Applied Physics Part 1 (1993), 32, 979).

Disclosure of the Invention

According to a first aspect, the present invention consists in an electrically semi-conducting or conducting composite material comprising a plurality of electrically insulating thermoplastic particles coated with

conducting or semiconducting polymer, the conducting or semiconducting polymer forming a network through the composite.

Preferably, the conducting or semiconducting polymer is soluble in organic or inorganic solvents and can comprise polyaniline or a polyaniline derivative. The polyaniline is preferably a doped polyaniline-camphorsulfonic acid in meta-cresol.

The difference between the glass transition temperature and melting temperature of the thermoplastic material is preferably greater than $20^{o}C$ thereby allowing pressing of the thermoplastic material in its rubbery state and avoiding melting and disruption of the morphology. In one embodiment, the thermoplastic material is an amorphous polymer. The thermoplastic can comprise unplasticised or plasticised poly(vinyl chloride) (PVC). The plasticiser is preferably any additive which lowers the glass transition temperature of the material and can include internal plasticisers or an ester plasticiser such as dioctyl phthalate or dibutyl phthalate.

The surface of the thermoplastic particles prior to coating with the conducting polymer is preferably treated to increase its wettability by the conducting or semiconducting polymer and so improve the adhesion between the coating and the particle. The surface treatment preferably comprises, plasma etching, chemical etching, or, most preferably, sulfonation in which sulfo groups, $-SO_3H$, are bonded to the surface of the particles. The thermoplastic particles are preferably approximately spherical in geometry with a diameter less than 100 microns. The particles may also contain ferromagnetic particles to enhance electromagnetic shielding.

The ratio of conducting polymer to thermoplastic material in the composite preferably lies in the range 0.1% w/w-20% w/w. The electrical conductivity of the composite preferably lies in the range 0.001-50 S/cm but can be varied over a larger range by appropriate doping of the conducting polymer. The percolation threshold of the composite is preferably less than 1% w/w of the conducting polymer.

According to a second aspect, the present invention consists in an electrically insulating thermoplastic particle substantially coated with a layer of a soluble conducting polymer. Preferably, the soluble polymer comprises a doped or undoped polyaniline or polyaniline derivative.

According to a third aspect, the present invention consists in a method for preparing an electrically semi-conducting or conducting

composite material comprising bringing together thermoplastic particles coated with conducting or semiconducting polymer under conditions of temperature such that the particles are bonded together or coalesced without destroying the connectivity of the conductive coatings to produce a conductive network.

The thermoplastic particles can be substantially spherical sulfonated poly(vinyl chloride) particles coated with a layer of doped polyaniline.

The temperature is preferably set between the glass transition temperature and the flow point of the thermoplastic. Where the thermoplastic is poly(vinyl chloride), the temperature is preferably set in the range 145°C to 155°C.

The thermoplastic particles are also preferably brought together under pressure, the pressure being sufficiently low so as to prevent shear stress deforming the particles to a point where the conducting or semiconducting polymer coating is disrupted. The pressure may be applied by pressing or extrusion of the material.

According to a final aspect, the present invention consists in a method for preparing a thermoplastic particle substantially coated with a layer of doped or undoped conducting polymer comprising the step of substantially coating the thermoplastic particle with a layer of doped or undoped conducting polymer.

The particles are preferably coated by mixing the particles with a solution containing dissolved doped or undoped conducting polymer followed by a drying of the particles, if necessary, at an elevated temperature and under vacuum.

The conducting polymer is preferably polyaniline, with the polyaniline solution preferably comprising a doped polyaniline-camphorsulfonic acid in meta-cresol.

The thermoplastic particles are preferably an amorphous polymer, such as poly(vinyl chloride) particles which have undergone a surface treatment prior to being mixed with the solution. The surface treatment preferably comprises a sulfonation process wherein sulfonate groups are bonded to the surface of the particles.

The sulfonated particles are pref rably soaked in a plasticiser prior to being mixed in the polyaniline solution. The plasticiser may comprise an ester plasticiser such as dioctyl phthalate or dibutyl phthalate. The addition

of the plasticiser results in a composite having improved mechanical characteristics such as flexibility without lowering the electrical conductivity.

The processability of the conducting thermoplastic composite improves its potential for use in a variety of applications. The composite can be utilised in a range of devices including microwave devices, pressure sensors, temperature sensors, cable shielding, magnetic shielding, anti-static materials for computers and other applications, radar-absorbing materials, light weight corrosion resistant electrodes, high-power junction devices and corrosion resistant cable termination coatings.

Brief Description of the Drawings

Figure 1 is an optical micrograph of 4% PAn-CSA/PVC pressed at 150°C/28MPa;

Figure 2 is an optical micrograph of 4% PAn-CSA/PVC pressed at 200°C/28MPa;

Figure 3 is a graph of electrical conductivity of the composite material as a function of loading of PAn-CSA/PVC;

Figure 4 is a graph of DMTA results for composite materials made according to the present invention having varying quantities of PAn-CSA/PVc: and

Figure 5 is a graph of DMTA results for composite materials made according to the present invention containing 4% PAn-CSA/PVC and varying amounts of plasticiser.

Best Method of Performing the Invention

By way of example only, a preferred embodiment of the invention is described below.

Example 1 - Sulfonation of poly(vinyl chloride) (PVC) and Preparation of Composite

To sulfonate the surface of the PVC particles, 50 grams of poly(vinyl chloride) particles having a diameter ranging from 50-110 microns were stirred with 200 millilitres of 15% oleum (namely, 15% by weight of SO_3 in anhydrous sulfuric acid) at room temperature for 2-3 minutes. The slurry was then filtered through a sintered glass funnel and successively washed with concentrated sulphuric acid (2 x 100 millilitres), 90% sulphuric acid (2 x 100 millilitres), 75% sulphuric acid (2 x 100 millilitres), 50% sulphuric acid, distilled water (5 x 100 millilitres) and finally methanol (2 x 100

millilitres). The resulting sulfonated poly(vinyl chloride) was then dried under vacuum for 24 hours. The degree of sulfonation was determined to be $1.6 \times 10^{10} SO_3$ groups/cm^2. The particles were then suspended in petroleum spirit (80-100°C fraction) (200 millilitres) containing dioctyl phthalate (DOP) (10 grams) and the solvent was allowed to slowly evaporate. The result was a plurality of sulfonated poly(vinyl chloride) spherical particles containing plasticiser.

To prepare the composite. 11.8 grams of a solution containing 3.4% w/w polyaniline-camphorsulfonic acid (PAn-CSA) (2:1 molar ratio) in meta-cresol was mixed thoroughly with 10 grams of the prepared sulfonated PVC particles. The resulting slurry was placed in a vacuum oven at 60-65°C and 2-5 torr for 16 hours. The afforded dark green particles were lightly ground in a mortar and pestle prior to pressing. A hydraulic press with the platens pre-heated to 150°C was used to press 5 grams of these particles at 20-28 MPa for 4 minutes in a 7 x 7 x 0.05 cm positive displacement die. Using the above ratio of polyaniline solution to poly(vinyl chloride) produced a composite containing 4% w/w polyaniline in poly(vinyl chloride).

<u>Experiments Performed on Prepared Composites</u>

The composite material as prepared using the process described in Example 1 had a conductive network of PAn-CSA 10 around the poly(vinyl chloride) (PVC) particles 20 as is clearly depicted in Figure 1. Pressing an identically prepared sample of composite at a temperature exceeding the flowpoint of the PVC (ie. at 200°C) resulted in destruction of the network morphology in the composite as is clearly depicted in Figure 2.

Further samples having varying weight fractions of PAn-CSA in PVC were prepared with the electrical conductivity of the composites being determined by the standard 4-probe measurement. The results are depicted in Figure 3. It can be readily seen from Figure 3 that the percolation threshold of the composite is less than 1% w/w PAn-CSA. As is depicted in Figure 3. the sample prepared using the method described in Example 1 was measured to have an electrical conductivity of 1.2 S/m using a standard 4-probe measurement.

The conducting composite prepared using the method defined in Example 1 while not having mechanical properties identical to PVC does have improved mechanical properties in comparison to intrinsically conducting polymers. DMTA studies in bending mode on samples prepared

as described in Example 1 but with varying quantities of PAn-CSA showed a substantial change in the softening temperature of the samples with increasing PAn-CSA loading. Softening occurs around 70°C for all samples (cf:90°C for PVC pressed in an identical manner). Notably, below 65°C there is almost no difference in modulus, the stiffness being comparable to that of PVC.

Further experiments were undertaken to explore the effect of plasticiser on the properties of the composite. Composite samples having varying levels of dioctyl phthalate (DOP) were prepared as described in Example 1. DMTA measurements in tensile mode on samples containing 4% PAn-CSA/PVC at varying amounts of DOP are shown in Figure 5. These results display a systematic decrease in the softening temperature (T_g) with the addition of DOP, as would be expected for a plasticised material.

At a DOP loading of greater than or equal to 30%, the conductivity of the composite is effected when pressed at 150°C, due to the low softening temperature (<50°C). The high processing temperature relative to the 30% DOP softening temperature leads to the destruction of the connective morphology shown in Figure 1, and the formation of a morphology similar to that shown in Figure 2.

The processability of the composite also allows the material to be employed in a wide range of applications as hereinbefore described.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

CLAIMS:

1. An electrically semi-conducting or conducting composite material comprising a plurality of electrically insulating thermoplastic particles coated with conducting or semiconducting polymer, the conducting or semiconducting polymer forming a network through the composite.

2. The composite material of claim 1 wherein the conducting or semiconducting polymer is soluble in organic or inorganic solvents.

3. The composite material of claim 1 wherein the conducting or semiconducting polymer is polyaniline or a polyaniline derivative.

4. The composite material of claim 1 wherein the thermoplastic polymer is an amorphous polymer.

5. The composite material of claim 1 wherein the thermoplastic material is unplasticised or plasticised poly(vinyl chloride) (PVC).

6. The composite material of claim 1 wherein the surface of the thermoplastic particles prior to coating with the conducting or semiconducting polymer undergoes a surface treatment to increase its wettability by the conducting or semiconducting polymer comprising chemical etching, plasma etching or sulfonation.

7. The composite material of claim 1 wherein the thermoplastic particles are approximately spherical with a diameter less than 100 microns.

8. The composite material of claim 1 wherein the ratio of conducting polymer or semiconducting polymer to thermoplastic material in the composite lies in the range 0.1% w/w-20% w/w

9. The composite material of claim 1 wherein the electrical conductivity of the composite lies in the range 0.001-50 S/cm.

10. The composite material of claim 1 wherein the percolation threshold of the composite is less than 1% w/w of conducting polymer.

11. An electrically insulating thermoplastic particle substantially coated with a layer of conducting or semiconducting polymer for use in making the composite of claim 1.

12. The particle of claim 11 wherein the layer of conducting or semi-conducting polymer encloses the surface of the particle.

13. The particle of claim 11 wherein the conducting or semiconducting polymer is soluble in organic or inorganic solvents.

14. The particle of claim 11 wherein the conducting or semiconducting polymer comprises a doped or undoped polyaniline or polyaniline derivative.

15. The particle of claim 11 wherein the thermoplastic material is an amorphous polymer.

16. The particle of claim 11 wherein the thermoplastic material is unplasticised poly(vinyl chloride) (PVC).

17. The particle of claim 11 wherein the thermoplastic material is plasticised poly(vinyl chloride) (PVC).

18. The particle of claim 11 wherein the surface of the particle prior to coating with the conducting or semiconducting polymer undergoes a surface treatment to increase its wettability by the conducting or semiconducting polymer comprising chemical etching, plasma etching or sulfonation.

19. The particle of claim 11 wherein the particle is approximately spherical with a diameter less than 100 microns.

20. A method for preparing an electrically semi-conducting or conducting composite material comprising bringing together thermoplastic particles coated with conducting or semiconducting polymer under conditions of temperature such that the particles are bonded together or coalesced without destroying the connectivity of the conducting coatings to produce a conductive network.

21. The method of claim 20 wherein the temperature is set between the glass transition temperature and the flow point temperature of the thermoplastic.

22. The method of claim 20 wherein the thermoplastic is an amorphous polymer.

23. The method of claim 20 wherein the thermoplastic is poly(vinyl)chloride (PVC).

24. The method of claim 23 where in the temperature is set in the range 145-155°C

25. The method of claim 20 wherein the thermoplastic particles are approximately spherical sulfonated poly(vinyl chloride) particles coated with a layer of doped polyaniline.

26. The method of claim 20 wherein the thermoplastic particles are also brought together under pressure, the pressure being sufficiently low so as to

prevent sheer stress deforming the particles to a point where the conducting or semiconducting polymer coating is disrupted.

27. The method of claim 26 wherein the pressure is applied by pressing or extrusion of the material.

28. A method for preparing a thermoplastic particle substantially coated with a layer of doped or undoped conducting polymer for use in the method defined in claim 20 comprising the step of mixing the particle with a solution containing dissolved conducting polymer followed by a drying of the particle.

29. The method of claim 28 wherein the conducting polymer is polyaniline, with the polyaniline solution comprising a doped polyaniline-camphorsulfonic acid in meta-cresol.

30. The method of claim 28 wherein the thermoplastic particle is an amorphous polymer.

31. The method of claim 30 wherein the amorphous polymer is poly(vinyl chloride).

32. The method of claim 30 wherein the thermoplastic particle has undergone a surface treatment prior to the coating of the conducting polymer.

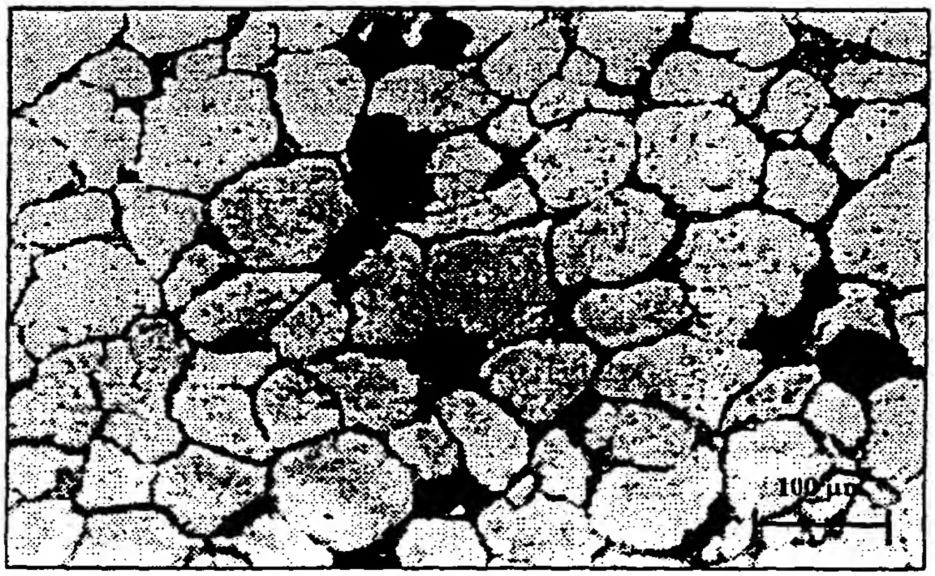


Figure 1

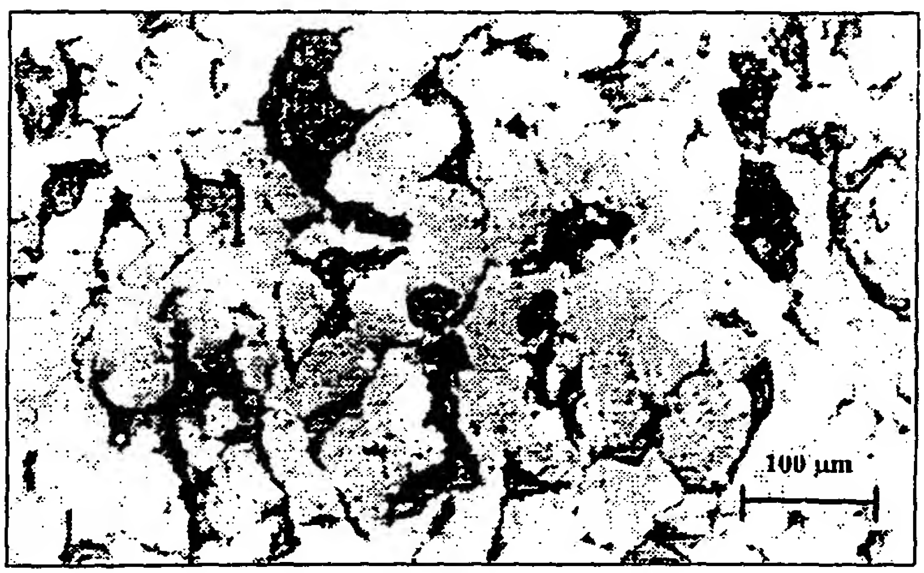


Figure 2

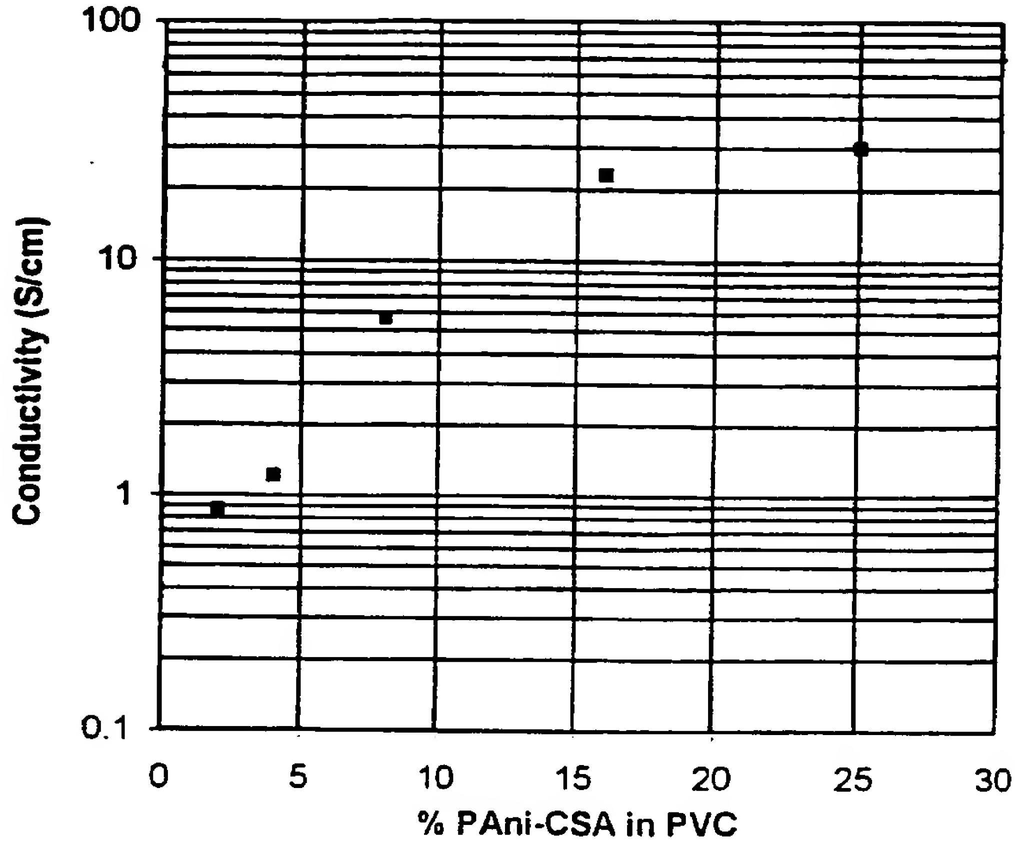
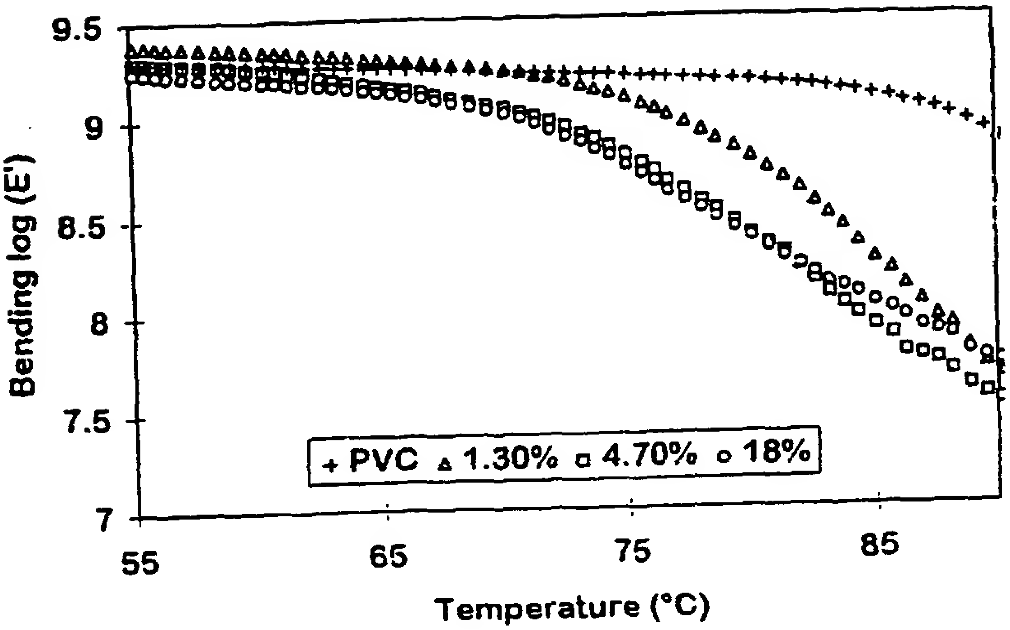


Fig. 3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65
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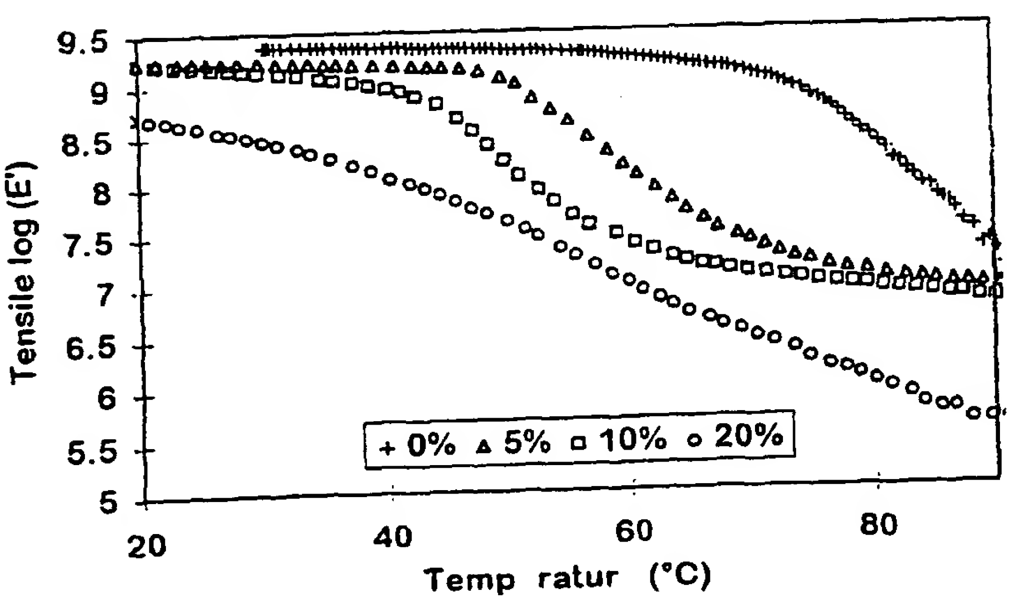
85
Temperature (°C)

Fig. 4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Temp ratur (°C)

Fig. 5

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00009

A.	**CLASSIFICATION OF SUBJECT MATTER**

Int Cl^{6}: C08J 3/20, C08L 27/22, B01J 13/22, H01B 1/12, H01L 51/30

According to International Patent Classification (IPC) or to both national classification and IPC

B.	**FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU:IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2616790 A (RHONE-POULENC) 23 December 1988 See abstract.	1, 11, 20
A	US 4517268 A (GRUBER) 14 May 1985 See examples on columns 7 and 8.	
X	Derwent Abstract Accession No. 94-104373/13, class V04, JP,A, 06052714 (JAPAN CARLIT) 25 February 1994	1, 11, 20

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